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(54) Method for forming film

(57) According to a method for forming a film based on a thermal CVD method, a fluorine-containing silicon oxide film is formed on a substrate (6) by virtue of thermal reaction of mixed gas under the condition where the substrate (6) is being heated. The mixed gas including organic silane having Si-F bond, organic silane having no Si-F bond, and ozone-containing gas.

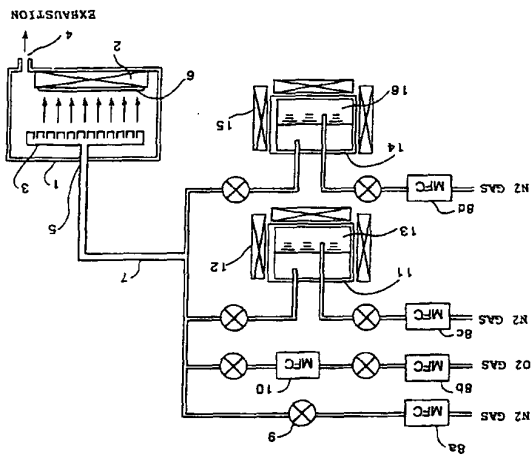


FIG. 1

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BACKGROUND OF THE INVENTION

Description

1. Field of the Invention

The present invention relates to a film forming method and, more particularly, a film forming method for forming a fluorine containing silicon oxide film in terms of a thermal CVD method.

2. Description of the Prior Art

In the prior art, most of interlayer insulating layer used for semiconductor devices are formed of SiO₂ film or SiO₂-based film. Such SiO₂-based insulating film is of a relative dielectric constant of about 4.0 (measuring frequency of 1 MHz). According to the above explanation, a capacitance C between upper and lower conductors sandwiching an interlayer layer, and between adjacent conductive layers putting the interlayer insulating film therebetween might be determined. In other words,

$$C = \epsilon_0 \cdot \epsilon \cdot A / t$$

Where

ϵ_0 : dielectric constant in vacuum (=1),
 ϵ : relative dielectric constant of interlayer insulating film,
 A: overlapping area of upper and lower interconnection layers or opposing areas between adjacent interconnection layers (How-
 ever, it has to be actually taken account that contribution of areas between the interconnection layers other than the overlapping area, otherwise contribution of areas other than the opposing area between the interconnection layers), and
 t: film thickness of the interlayer insulating film disposed between the upper and lower interconnection layers, or a space formed between adjacent interconnection layers sandwiching the interlayer insulating film.

Such parasitic capacitance resides in any kind of semiconductor device. However, if a value of such parasitic capacitance is considerably large, either a crosstalk between the interconnection layers would occur or delay would be caused in signal propagation time. In particular, if a multilayered structure is utilized in order to achieve high integration density of the semiconductor device, parasitic capacitance would be increased since overlapping areas or opposing areas between the interconnection layers are increased. Furthermore, since a space between the adjacent interconnection layers is narrowed if dimensions of the patterns are made fine,

(1) Using an organic resin film, it has been reported that the interlayer insulating film of the relative dielectric constant of less than $\epsilon = 3.0$ is used.
 (2) Using a Teflon-based insulating film. The interlayer insulating film of the relative dielectric constant of less than $\epsilon = 3.0$ has been reported.
 (3) Using an SiBN film or SiOBN film. An example has been reported in which the interlayer insulating film is formed by sputtering.
 (4) Using either an SiO₂ film with Si-F bond or SiO₂ film including F.

As one approach for reducing the parasitic capacitance on the device characteristics cannot be ignored. Therefore influence of the parasitic capacitance is increased. For this reason, the parasitic capacitance the space between the upper and lower interconnection layers. cent interconnection layers become small rather than there are some cases where the space between adjacent interconnection layers becomes small rather than the space between the upper and lower interconnection layers. For this reason, the parasitic capacitance is increased. Therefore influence of the parasitic capacitance on the device characteristics cannot be ignored. As one approach for reducing the parasitic capacitance, it may be considered to reduce the relative dielectric constant (ϵ) of the interlayer insulating film. Currently, the followings are taken as countermeasures.

However, in the cases of (1) and (2), since the interlayer insulating film is formed of the substance which is totally different from SiO₂, sufficient reliability and stability of the film cannot be achieved. In addition, evaluation for its application to the devices has not progressed, and therefore applicability of such insulating film is not certain or confirmed in practical use.
 In turn, in the cases of (3), since such insulating film has high hygroscopicity, it is not suitable for application to the semiconductor device. Moreover, this is a method for forming a BSG film by causing SiOB source (organic compound having SiOB bond, for instance, trimethylsilylborate) to react with ozone to form the BSG film, which is in the middle of research and development. Besides, in the cases of (4), the fluorine (F) - containing silicon oxide film may be formed by various ways, and technique for providing about 3.4 to 3.6 as the value of relative dielectric constant (ϵ) is being investigated and developed. At all events, it is important to form the fluorine - containing silicon oxide film which is stable in quality.
 In the prior art, the followings may be exemplified as the method for forming the fluorine - containing silicon oxide film.

(1) Hydrolysis of fluorotriethoxysilane (SiF(OC₂H₅)₃).
 (2) Plasma CVD method using triethoxysilane (TEOS), C₂F₆, and oxygen (O₂).
 (3) Plasma CVD method or ECR plasma CVD method using SiF₄ and oxygen (O₂), and
 (4) Plasma CVD method using SiF(OC₂H₅)₃ and oxygen (O₂).
 In the above methods, the plasma CVD method is employed as the film forming method except for the

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view showing a film forming apparatus for use in formation of a fluorine - containing silicon oxide film according to an embodiment of the present invention;

FIG. 2 is a schematic view showing a plasma processing apparatus for use in plasma processing of the fluorine - containing silicon oxide film according to the embodiment of the present invention;

FIG. 3 is a characteristic view illustrating a relationship between deposition rate and deposition temperature of the fluorine - containing silicon oxide film formed by a film forming method according to the embodiment of the present invention;

FIG. 4 is a characteristic view illustrating a relationship between deposition rate and flow rate of F₂ of the fluorine - containing silicon oxide film formed by the film forming method according to the embodiment of the present invention;

FIG. 5 is a characteristic view illustrating a relationship between refractive index and deposition rate of F₂ of the fluorine - containing silicon oxide film formed by the film forming method according to the embodiment of the present invention;

FIG. 6 is a characteristic view illustrating a relationship between refractive index and flow rate of F₂ of the fluorine - containing silicon oxide film formed by the film forming method according to the embodiment of the present invention;

FIG. 7 is a characteristic view illustrating the results of infrared absorption in the fluorine - containing silicon oxide film formed by the film forming method according to the embodiment of the present invention;

FIG. 8 is a characteristic view illustrating a quality improving effect due to the plasma irradiation process on the fluorine - containing silicon oxide film formed by the film forming method according to the embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A film forming system which is used to form a fluorine - containing silicon oxide film according to an embodiment of the present invention will be explained at first hereinafter with reference to FIG. 1.

FIG. 1 is a schematic view showing a configuration of a thermal CVD apparatus comprising a reaction gas supplying section and a film forming section.

As shown in FIG. 1, a water loading table 2 having a built-in heater therein and a gas discharging portion 3 are furnished with a film forming chamber 1. An exhaust port 4 and a gas introducing port 5 are provided in the film forming chamber 1. Reaction gas is introduced from the gas introducing port 5 into the film forming chamber 1 via a pipe 7 while unnecessary reaction gas is exhausted from the exhaust port 4 to the outside of the

method (1). The values $\epsilon = 3.4$ to 3.6 of relative dielectric constant have already been achieved by these methods.

However, these fluorine containing silicon oxide films are prone to absorb moisture, as a result of which a relative dielectric constant of the silicon oxide films is increased. In other words, the silicon oxide films are inferior in water resistance.

In particular, if being formed by the plasma CVD method, the silicon oxide films exhibit poor step coverage, so that they are not suitable to be filled into minute spaces. Although ECR plasma CVD method is the most stable one of various plasma CVD methods, it is not fitted for mass production because of its large scaled equipment. In addition, SiF₄(OC₂H₅)₃ has Si-F bond originally as source material, but it is difficult to keep the bond in the plasma as it is and therefore it is hard to accomplish the silicon oxide film in which fluorine is contained properly by controlling fluorine density.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a film forming method capable of forming a fluorine - containing silicon oxide film which is superior in step coverage, of a small relative dielectric constant, and stable in film quality.

In the present invention, organic silane having Si-F bond is used as a source gas by the inventors. This source gas is extremely easy to be decomposed, and thus hydrolysis and oxidation reaction of the source gas are caused at the normal temperature. In order to suppress such decomposition, organic silane having no Si-F bond has to be added to the source gas in proper quantity. The fluorine - containing silicon oxide film is formed by virtue of reaction of the source gas with ozone in the situation where a substrate is being heated. At this time, it is preferable that the substrate temperature is held in the range of 300 to 400 °C to accomplish proper deposition rate and good quality of the silicon oxide film.

In the fluorine - containing silicon oxide film formed as mentioned above, relative dielectric constant can be controlled according to an amount of contained fluorine. As a rule, the more an amount of contained fluorine, the lower the relative dielectric constant. Since the fluorine - containing silicon oxide film is formed by thermal CVD method, it is superior in step coverage.

Furthermore, with the use of reforming process for exposing the fluorine - containing silicon oxide film to oxygen or nitrogen plasma, moisture contained in the film can be removed to thus lower the relative dielectric constant much more. In addition, denseness of the silicon oxide film can be increased by plasma irradiation process to thus result in increased water resistance of the silicon oxide film. Consequently, variation in the relative dielectric constant with elapsed time can be suppressed and therefore low relative dielectric constant can be maintained.

film forming chamber 1. Mixed reaction gas is supplied to the pipe 7 from the reaction gas supplying portion. The reaction gas supplying portion is equipped with a plurality of branch pipes which are connected to respective gas sources corresponding to gas to be used. In the embodiment of the present invention, the branch pipes comprise a first branch pipe for supplying nitrogen gas, a second branch pipe for supplying ozone (O₃) containing oxygen gas, a third branch pipe for supplying organic silane with Si-F bond, e.g., fluorotriethoxysilane (F-TES), and a fourth branch pipe for supplying organic silane without Si-F bond, e.g., tetraethoxysilane (TEOS).

To the first branch pipe are provided a port for introducing nitrogen gas, a mass flow controller (MFC) 8a, and a switching valve 9 which may cut off/introduce gas flow. In the course of the second branch pipe between a port for introducing oxygen gas and the pipe 7 are interposed a mass flow controller (MFC) 8b, an ozone generating unit 10, and switching valves 9 which may cut off/introduce gas flow. The ozone generating unit 10 may convert oxygen gas into ozone in proper quantity so as to adjust the ozone density in oxygen gas.

To the third branch pipe are provided an introducing port for carrier gas (nitrogen gas), a mass flow controller (MFC) 8c, a container 11 containing F-TES solution 13 therein, a heater 12 for heating the F-TES solution 13, and switching valves 9 which may cut off/introduce gas flow. Nitrogen gas including F-TES in virtue of bubbling of the carrier gas (nitrogen gas) can be supplied to the pipe 7.

In the middle of the fourth branch pipe between a port for introducing carrier gas (nitrogen gas) and the pipe 7 are interposed a mass flow controller (MFC) 8d, a container 14 containing TEOS solution 16 therein, a heater 15 for heating the TEOS solution 16, and switching valves 9 which may cut off/introduce gas flow. Nitrogen gas including TEOS in virtue of bubbling of the carrier gas (nitrogen gas) can be supplied to the pipe 7. Subsequently, referring to FIG. 1, there will be explained a method for forming the fluorine - containing silicon oxide film according to the embodiment of the present invention based on an atmospheric pressure CVD method.

First a water 6 is placed on the water loading table 2 positioned at the bottom of the film forming chamber 1 and then heated. For purposes of experiment, the temperature of the water 6 is varied film by film within the range of 100 to 350 °C.

In turn, the F-TES solution 13 is heated and then held at the temperature of 40 °C. At the same time, the TEOS solution 16 is heated and then held at the temperature of 65 °C.

Next, all switching valves 9 provided on respective branch pipes are opened. More particularly, nitrogen gas is supplied at flow rate of 18 SLM to the pipe 7 via the first branch pipe, oxygen gas including ozone by 2.4 % is supplied at flow rate of 7.5 SLM to the pipe 7 via the second branch pipe, nitrogen gas including F-TES is

supplied to the pipe 7 via the third branch pipe, and nitrogen gas including TEOS is supplied at flow rate of 2.0 SLM to the pipe 7 via the fourth branch pipe. These gases are then mixed and supplied to the film forming chamber 1. For purposes of experiment, flow rate of nitrogen gas including F-TES is varied within the range of 0.5 to 3.0 SLM.

Mixed gas is discharged toward the water 6 from the gas discharging portion 3 in the film forming chamber 1 to start film forming processes. With holding such condition for a predetermined time, the fluorine - containing silicon oxide film is formed on the water 6 to have a predetermined thickness.

FIG. 3 shows a correlation of the deposition rate with the deposition temperature. An ordinate represents the deposition rate (nm/min) in linear scale while an abscissa represents the deposition temperature (°C) in linear scale. The flow rate of F-TES is kept constant at 2.0 SLM. As shown in FIG. 3, the deposition rate assumes its maximum value of about 250 nm/min at almost 250 °C.

FIG. 5 shows a relationship between the refractive index of the fluorine - containing silicon oxide film obtained and the deposition temperature. An ordinate represents the refractive index in linear scale while an abscissa represents the deposition temperature (°C) in linear scale. The flow rate of F-TES is maintained constant at 2.0 SLM.

As shown in FIG. 5, the refractive index is about 1.385 at the deposition temperature of 180 °C. The refractive index is then increased linearly with the increase in the deposition temperature. Finally the refractive index becomes about 1.425 at the substrate temperature of 350 °C.

With this change of the refractive index, it can be understood that fluorine is hard to be introduced in the film as the deposition temperature is increased. In other words, the lower the deposition temperature, the smaller the refractive index.

A relationship between the flow rate of F-TES and the deposition rate is shown in FIG. 4. An ordinate represents the deposition rate (nm/min) in linear scale while an abscissa represents the flow rate of F-TES (SLM) in linear scale. The substrate temperature is held constant at 280 °C.

As shown in FIG. 4, the deposition rate is increased linearly with the increase in flow rate of F-TES, and the deposition rate reaches about 230 nm/min at the flow rate of F-TES of 3.0 SLM.

FIG. 6 shows a relationship between the refractive index of the fluorine - containing silicon oxide film formed and the flow rate of F-TES. An ordinate represents the refractive index in linear scale while an abscissa represents the flow rate of F-TES (SLM) in linear scale. The substrate temperature is kept constant at 280 °C.

As shown in FIG. 6, the refractive index is about 1.42 at the flow rate of F-TES of 0.5 SLM. The refractive index is then decreased gradually with the increase in

elapsed time can be suppressed and therefore low relative dielectric constant can be maintained.

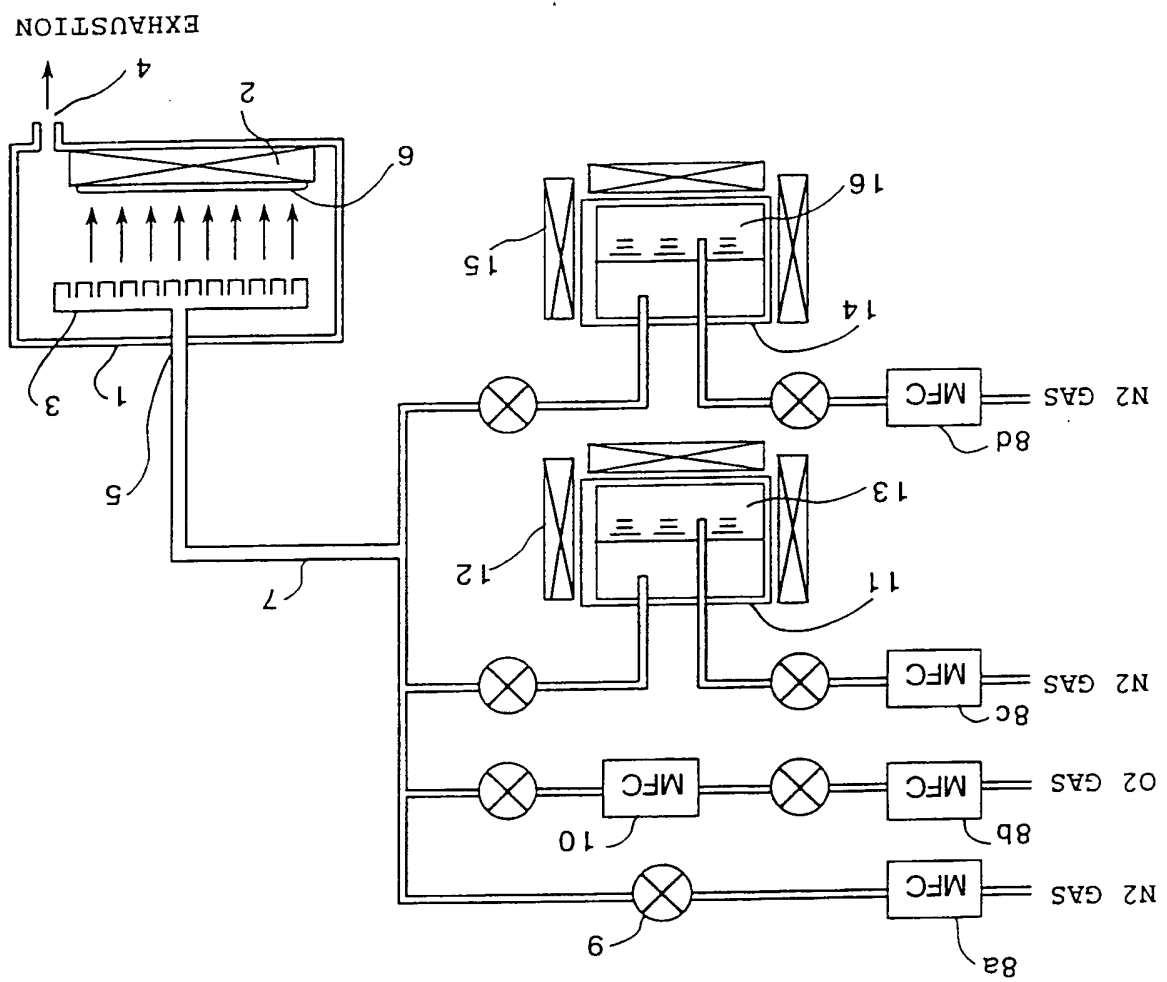
the flow rate of F-TES. Finally the refractive index becomes about 1.36 at the flow rate of F-TES of 3.0

oxygen or nitrogen plasma, moisture contained in the film can be removed. In addition, denseness of the silicon oxide film can be increased by plasma irradiation process to thus increase water resistance of the silicon oxide film. Thereby, variation in the relative dielectric constant with elapsed time can be suppressed and therefore low relative dielectric constant can be maintained.

Claims

1. A method for forming a film comprising the step of forming a fluorine-containing silicon oxide film on a substrate (6) by means of thermal reaction of mixed gas while said substrate (6) is being heated, said mixed gas including organic silane having Si-F bond, organic silane having no Si-F bond, and ozone-containing gas.
2. A method for forming a film according to claim 1, wherein said fluorine-containing silicon oxide film is formed at atmospheric pressure.
3. A method for forming a film according to claim 1 or 2, wherein said organic silane having Si-F bond is composed of fluoroalkoxysilane ($(\text{SiF}_n(\text{OR})_{4-n})$, $n=1$ to 3, R is alkyl group, aryl group, or their derivative), fluoroalkylsilane ($(\text{SiF}_n\text{R}_{4-n})$, $n=1$ to 3, R is alkyl group, aryl group, or their derivative), chain fluorosiloxane ($(\text{R}_n\text{F}_{3-n}\text{SiO})_m\text{SiF}_{3-n}\text{R}_n$, $n=1, 2$, $k=0$ to 2, $m \geq 0$, R is alkyl group, aryl group, or their derivative), or ring fluorosiloxane ($(\text{R}_k\text{F}_{2-k}\text{SiO})_m$, $k=1, m \geq 2$, R is alkyl group, aryl group, or their derivative).
4. A method for forming a film according to claim 1 or 2, wherein said organic silane having no Si-F bond is composed of alkoxysilane ($(\text{SiH}_n(\text{OR})_{4-n})$, $n=1$ to 3, R is alkyl group, aryl group, or their derivative), alkylsilane ($(\text{SiH}_n\text{R}_{4-n})$, $n=1$ to 3, R is alkyl group, aryl group, or their derivative), chain siloxane ($(\text{R}_n\text{H}_3\text{SiO})_m\text{SiH}_{3-n}\text{R}_n$, $n=1, 2$, $k=0$ to 2, $m \geq 0$, R is alkyl group, aryl group, or their derivative), or ring siloxane ($(\text{R}_k\text{H}_{2-k}\text{SiO})_m$, $k=1, m \geq 2$, R is alkyl group, aryl group, or their derivative).
5. A method for forming a film according to claim 1, 2, 3 or 4, wherein said ozone-containing gas is composed of ozone (O_3) and oxygen (O_2).
6. A method for forming a film according to claim 1, further comprising the step of exposing said fluorine-containing silicon oxide film to plasma including at least one of oxygen and nitrogen under the condition where said substrate is being heated after said fluorine-containing silicon oxide film is formed on said substrate.
7. A method for forming a film according to claim 6,

FIG. 1



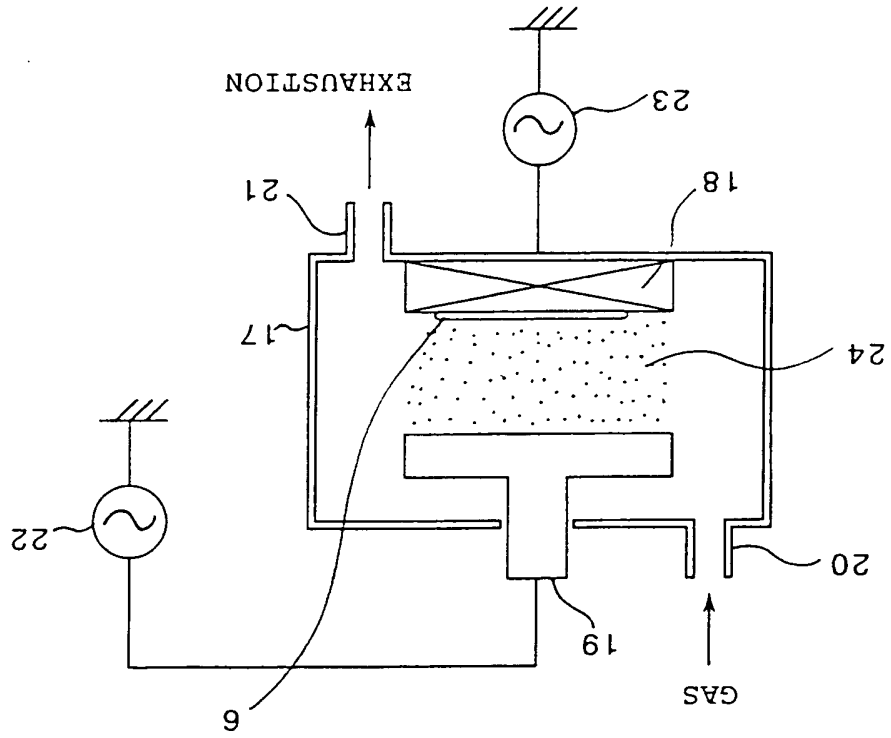


FIG. 2

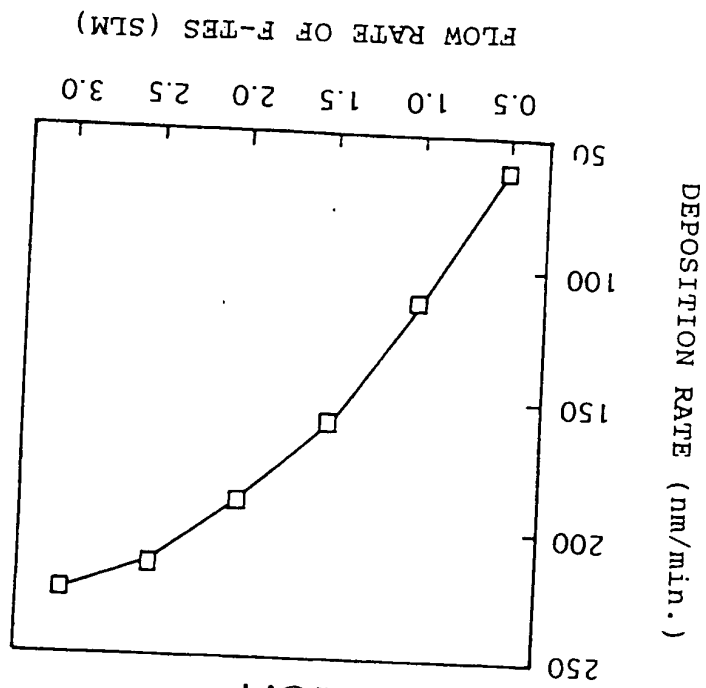


FIG.4

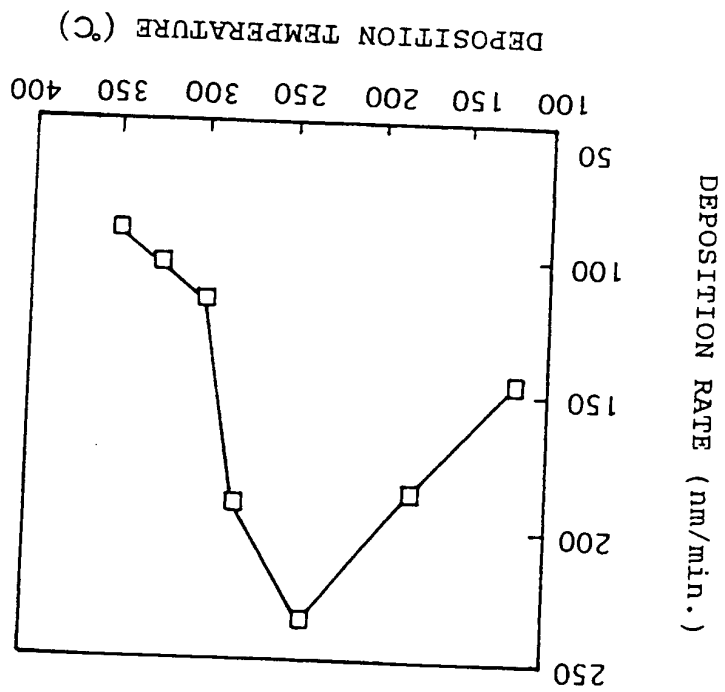


FIG.3

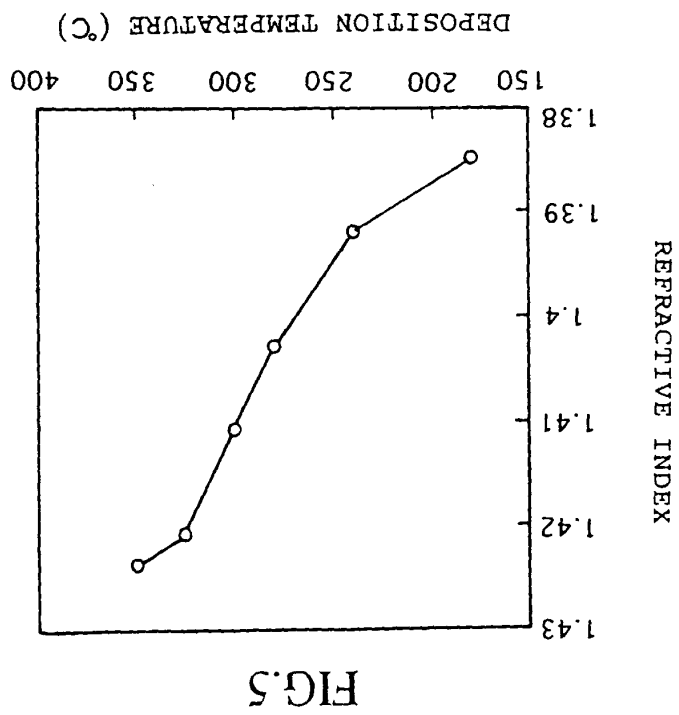


FIG. 5

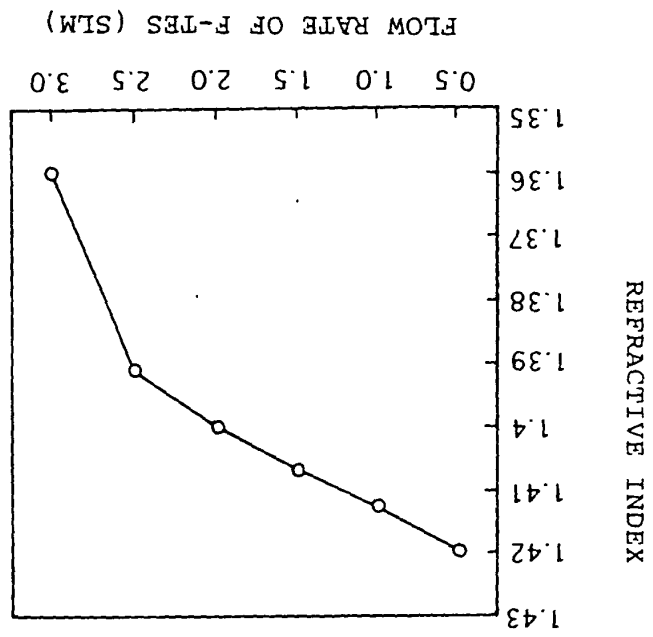


FIG. 6

FIG.7

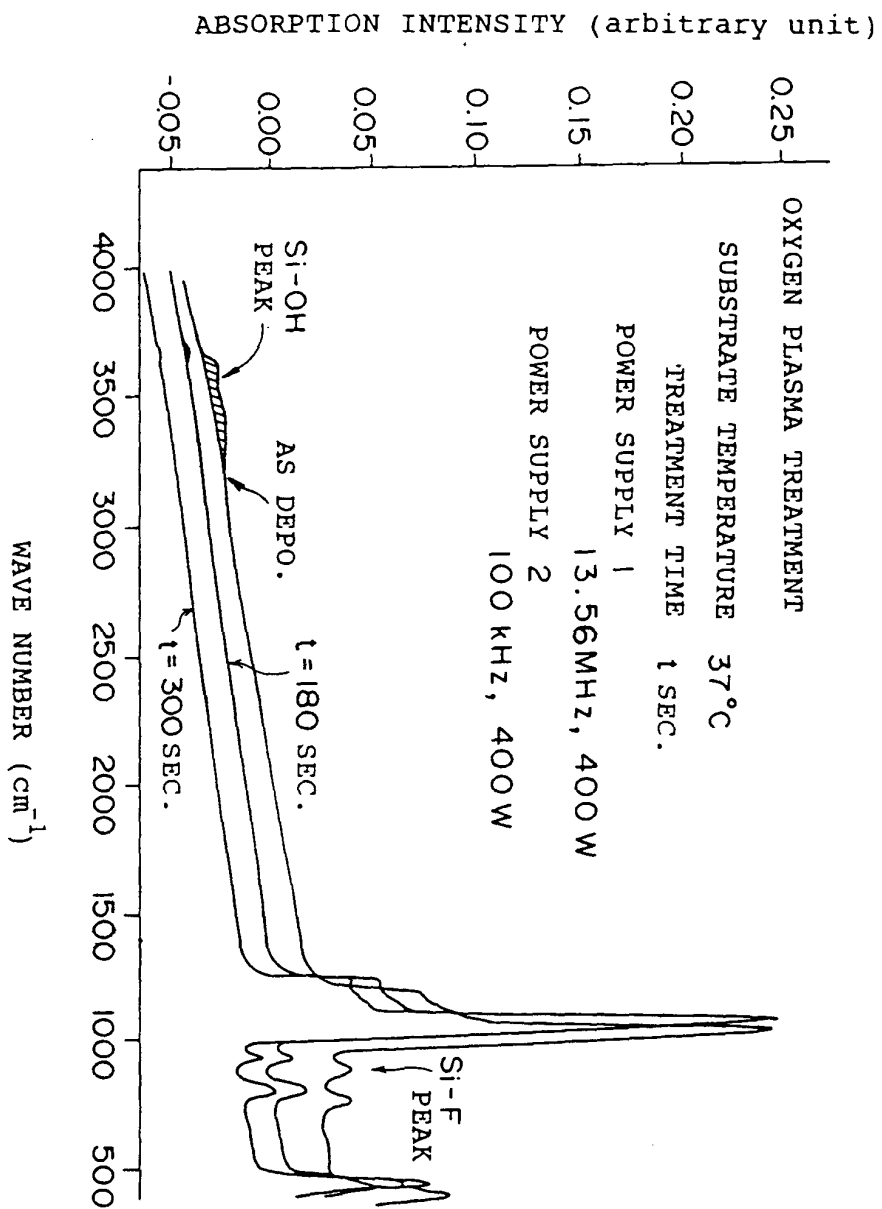


FIG.8

SOURCE MIXING RATIO (F-TES TO TES)	DEPOSITION TEMPERATURE (°C)	UPPER ELECTRODE (13.56MHz)	LOWER ELECTRODE (100KHz)	TREATMENT CONDITION (FOR EXPOSING TO PLASMA)	RELATIVE DIELECTRIC CONSTANT (ϵ , 1MHz)	REFRACTIVE INDEX (Nf)
1:1	350	400W	400W	O ₂	3.5-3.7	1.414
1:1	300	400W	400W	O ₂	3.8-3.9	1.419
2:1	300	400W	400W	O ₂	3.2-3.4	1.420
2:1	350	WITHOUT EXPOSING TO PLASMA			> 4	1.429
2:1	300	WITHOUT EXPOSING TO PLASMA			> 4	1.420
1:1	350	400W	400W	N ₂	3.8-4.1	1.421
1:1	300	400W	400W	N ₂	3.6-4.0	1.433

(NOTE) TES : Triethoxysilane (SiH(OC₂H₅)₃)

EUROPEAN SEARCH REPORT

European Patent
Office



DOCUMENTS CONSIDERED TO BE RELEVANT

Citation of document with indication, where appropriate, of relevant passages		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Incl.6)
Category	The present search report has been drawn up for all claims		
X	EP-A-0 517 548 (NIPPON ELECTRIC CO) 9	1-3,5	C23C16/40
Y	December 1992 * column 2, line 44 - column 3, line 13 *	4	C23C16/30
X	EP-A-0 654 545 (APPLIED MATERIALS INC) 24	1	C23C16/56
	May 1995 * column 3, line 1 - line 21 *		
Y	US-A-5 429 995 (NISHIYAMA YUKIO ET AL) 4	4	
	July 1995 * column 7, line 16 - line 47 *		
A	EP-A-0 572 704 (SEMICONDUCTOR PROCESS LAB CO L; ALCAN TECH CO INC (JP); CANON SALE) 6,7		
	8 December 1993 * column 11, line 1 - line 49 *		
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		3 December 1996	Ekhu1t, H
CATEGORY OF CITED DOCUMENTS			
T : theory or principle underlying the invention, but published on, or after the filing date D : document cited in the application I : document cited for other reasons A : technological background U : non-written disclosure P : intermediate document X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category			
S : member of the same patent family, corresponding document			

